USEPA MRID 48072902

Washoff/Runoff of Cypermethrin Residues from Slabs of External Building Material Surfaces Using Simulated Runoff

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Guideline: Non-guideline residue study

Statements: The study was conducted in compliance with Good Laboratory Practice pursuant to 40 CFR Part 160.

Classification: This study is **Supplemental**. The results of the washoff study, in relative terms of percent of applied mass, can be used to qualitatively discuss the propensity for cypermethrin to washoff of different building materials. There was significant material loss in the field spikes therefore absolute concentrations should not be used from this study.

PC Code: 109702

Final Reviewer: Reuben Baris
Environmental Scientist

USEPA/OPP/EFED/ERB6 **Date:** April 3, 2012

Final Reviewer: José L. Meléndez,
Chemist

USEPA/OPP/EFED/ERB5 **Date:** April 3, 2012

Executive Summary

The objective of the study was to examine the potential for simulated rain to wash off a pyrethroid (cypermethrin) that had been applied to different external building materials using two representative product formulations (emulsifiable concentration (EC) and wettable powder (WP)). Building materials selected for this study were those typically used for construction of residential/urban structures in California that may receive applications of pyrethroids. Ten building material slabs were made of the following materials: clean unpainted concrete, clean painted concrete, clean unpainted stucco, clean painted stucco, clean aluminum siding, clean vinyl siding, clean unpainted wood, clean painted wood, painted wood with a dusty surface, and clean asphalt. Cypermethrin formulated as Cynoff® EC and Cynoff® WP Insecticides was applied a rate of 0.00062 fl oz/ft^2 (26.5 mg a.i./slab) and 0.00066 fl oz/ft^2 (28.1 mg a.i./slab), respectively to the building material slabs.

A rectangular slab (9 in. wide by 24 in. long) of each building material was assigned to each of three groups per formulation (three slabs as replicates per formulation) along with a control slab for the study (clean aluminum siding). Cypermethrin (respective formulations) was applied using a laboratory research track sprayer located at the University of Illinois, Champaign Urbana, Illinois. Following application, slabs were allowed to dry for 24-hrs after which slabs were transported to a separate indoor laboratory rainfall simulator facility at the University of Illinois. For each of the six, one-hour, one-inch-per-hour rainfall events, the test slabs were placed at a 30-degree angle from vertical. Test slab locations were randomly positioned on the simulator test floor. Water samples were transported on wet ice to the analytical laboratory, preserved and analyzed for cypermethrin using gas chromatography-negative chemical ionization mass spectrometry (GC-MS/NCI) method. Field spike or transit samples were spiked with nominal concentration of 1.03 ppb, and there was significant material loss with recoveries ranging from 49-62%. The limit of quantitation (LOQ) was 1.03 µg/L (approximately 0.01% of the applied).

Washoff quantified as percent of applied mass of cypermethrin ranged from <0.01 to 16.8% for Cynoff® EC and 0.07 to 11.3% for Cynoff® WP. Clean vinyl siding had the highest percent of applied cypermethrin in runoff (for both EC and WP formulations), whereas clean unpainted stucco test slabs had the least amount of cypermethrin in washoff. All building materials had similar runoff volumes except for the clean asphalt which was lower by comparison; variations in runoff volume between slabs in different treatment groups were due primarily to the position in the rainfall simulator. Clean vinyl siding, clean unpainted wood, and clean aluminum siding slab materials had greater statistically significant mean percent washoff of applied mass compared to the control (for both formulation types). Further, Cynoff® WP Insecticide had greater washoff as percent of applied cypermethrin compared to Cynoff® EC formulation.

I. Material and Methods

A. Materials

1. Test Material:

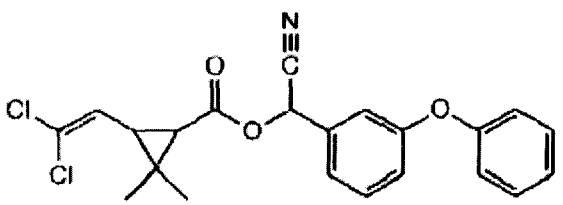
Product identification

Trade name: Cynoff® EC Insecticide
Type of formulation: Emulsifiable Concentrate
Active substance content: 24.8% cypermethrin
Proposed use: Insecticide
EPA reg. no.: 279-3081
Common name: Cypermethrin
Chemical name: (±) α-cyano (3-phenoxyphenyl) methyl (±) cis/trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate
CAS registration no.: 52315-07-8

Product identification
Trade name: Cynoff® WP Insecticide
Type of formulation: Wettable Powder
Active substance content: 40% cypermethrin
Proposed use: Insecticide
EPA reg. no.: 279-3070
Common name: Cypermethrin
Chemical name: (±) α-cyano (3-phenoxyphenyl) methyl (±) cis/trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate
CAS registration no.: 52315-07-8

Additional details about the test substances, storage, and shipment are provided on page 14 of the study report.

2. Chemical Structure of Cypermethrin



B. Methods

1. Site Conditions/Location

a. Study Site and Conditions (extracted from pg. 11 of the study report)**:**

The study was conducted at two indoor laboratory locations; a research laboratory track sprayer and laboratory rainfall simulator. Both facilities are located at the University of Illinois. The track sprayer equipment consisted of an open topped stainless steel booth with an exhaust vent and operable glass viewing and access doors. Applications were completed using a spray nozzle mounted on a traveler which moved side to side within the spray booth the length of the area of application. The track sprayer allowed for uniform delivery of cypermethrin to each slab. Following preparation of each slab surface to remove any potential surface residues (washing, soaking, and drying, see section 4.2 of study report), each slab, except the control, was

transported individually to the laboratory track sprayer. After application slabs were transported by vehicle in closed containers from the track sprayer location to the rainfall simulator location, allowed to dry for 24 hours, stored overnight in the locked rainfall simulator laboratory.

The laboratory rainfall simulator is a three-story indoor laboratory located at the University of Illinois. The simulator consisted of two parallel emitter modules, which allowed computer controlled nozzles to pass over calibrated openings in the modules. Rainfall was applied at the rate specified with a droplet size speed and energy representative of natural rainfall.

b. Selection and Construction of Building Materials

Building materials selected for this study were those typically found in California on areas of structures that may receive applications of pyrethroids. Ten building material slabs of different composition designed for this study were 9 inches wide by 24 inches long with varying depths depending on the material type. Table 1 lists the building material of each of the ten slabs.

Table 1. List of Building Materials Used for the Study (extracted from page 13 of the study report).

Slab Type	Source	Surface Finish	Details
Clean Unpainted Concrete (CUC)	Blager Concrete, Urbana, IL	Smooth concrete	Steel trowelled to a smooth finish
Clean Painted Concrete (CPC)	Blager Concrete, Urbana, IL	Painted smooth concrete	Latex satin finish porch and floor paint applied with a roller
Clean Unpainted Stucco (CUS)	Mixture of sand, Portland cement, Type S mortar, distilled water (individual materials obtained from The Home Depot Store #1984)	Pulled trowel textured surface	Smooth top coat followed by a gentle pulling motion that creates a typical stucco surface texture
Clean Painted Stucco (CPS)	Mixture of sand, Portland cement, Type S mortar, distilled water (individual materials obtained from The Home Depot Store #1984)	Same as clean unpainted stucco except painted	Latex semi-gloss exterior paint applied with a roller
Clean Aluminum Siding (CAL)	The Home Depot Store #1984 (SKU# 093346112445)	White semi-gloss factory finish	Pre-painted aluminum roll-stock
Clean Vinyl Siding[1] (CVL)	Menards, Champaign, IL (SKU#146-1389)	White faux wood finish	Vinyl soffit material
Clean Unpainted Wood (CUW)	Armstrong Cash and Carry Lumber Company, Urbana, IL (545 Clear Cedar)	Sanded clear cedar	Clean sanded surface with no knots or imperfections
Clean Painted Wood (CPW)	Armstrong Cash and Carry Lumber Company, Urbana, IL (545 Clear Cedar)	Painted over sanded clear cedar	Latex semi-gloss exterior paint applied with a roller
Painted Wood with a Dusty Surface (DPW)	Armstrong Cash and Carry Lumber Company, Urbana, IL (545 Clear Cedar)	Same as clean painted wood except the surface was left dusty	After paint drying a California soil was rubbed onto the surface, loose material was removed and the surface misted with water leaving a dusty painted surface
Clean Asphalt (ASP)	Open Road Asphalt, Inc. Fairmount, IL. (Bituminous Mix-85BIT4822)	Typical asphalt finish for driveways or roads	Tamped and compacted with a vibratory compactor

[1] Vinyl siding was not available with a nine-inch width. The only vinyl base material available was soffit stock that included two small notched channels formed into the material to mimic the look of three boards side by side.

Additional detail on the construction of each slab is provided on page 12 of the study report.

The goal of the study was to hold each building material slab at a 30-degree angle from vertical relative to its long dimension. The angle was chosen to ensure that rainfall came into contact with the slab surface to generate runoff for collection. Eleven slab stands (10 test stands and one control stand) were constructed from welded angle iron to support the range of test slab weights and hold the slabs at a consistent 30-degree angle and support the collection bottles in the correct position below the collection device.

c. Preparation of Building Material Surfaces for Application

Prior to application each building material was cleaned and prepared for application. Table 2 lists the preparation method for each building material.

Table 2. Preparation of Each Building Material Prior to Application

Slab Type	Preparation Method[†]	Comment
Clean Unpainted Concrete (CUC)	Soaked in water for at least 2 days (closed container)	To remove any substances from surface that might affect the pH of slab surface. Pyrethroids are known to hydrolyze at alkaline pHs.
Clean Painted Concrete (CPC)	Pre-rinsed using finished tap water, air dried day prior to application.	--
Clean Unpainted Stucco (CUS)		--
Clean Painted Stucco (CPS)		--
Clean Vinyl Siding (CVL)		--
Clean Aluminum Siding (CAL)		--
Clean Unpainted Wood (CUW)		--
Clean Painted Wood (CPW)		--
Asphalt (ASP)	Cleaned several days prior to application by brushing an Alconox Liqui-Nox detergent solution.	Method was done on vertical edges and slab surface to improve slab side condition by removing excess tar and oil and then rinsed with finished tap water.
Painted Wood with a Dusty Surface (DPW)	Rinsed with finished tap water to clean surface. After drying soil was poured and rubbed onto surface of slab.	Soil consisted of fine particles and larger clod aggregate. Excess soil was removed from surface by gravity after tipping each slab. Distilled water in a fine mist was applied to the surface to set the soil in place. Soil was analyzed by the laboratory for cypermethrin and less than 0.1 ppb (study authors reported this did not affect the results of the study).

[†]Muriatic acid (31.45% HCl) was added to each container every day during soaking to lower the pH of the water and slab surface. Illinois American Water Company in Urbana stated normal city water is maintained at a pH between 8.5 and 9.0. pH measurements after 48 hours in each container soaking the slabs was less than neutral. No cypermethrin was detected in finished water from the city of Urbana.

d. Application of Test Substance

A laboratory track sprayer located at the University of Illinois was used for the broadcast application of cypermethrin to the slabs in this study. The track sprayer was calibrated to deliver

a predetermined exact spray volume at a specific application rate to every slab. Spray height was maintained at 12-inches from the slab surface to the spray nozzle (platform height was adjusted for varying thickness of slab materials). Additional detail on the sprayer equipment is provided in section 4.3 of the study report (page 15-16 of the study report).

Application of Cynoff EC Insecticide and Cynoff WP insecticide to building material slabs was applied at the maximum label rate of one gallon per 400 ft^2 (0.2% solution of cypermethrin). The corresponding mass of cypermtherin is 26.5 mg per slab for the EC formulation, and 28.1 mg per slab for the WP formulation. A single tank mixture was prepared and applied to three groups (each containing one set of the ten building materials). Mass verification samples (petri dishes) were taken with each application to a slab material. Application monitoring samples were also taken to verify the target application rate. They consisted of petri dish-lids lined with filter paper.

Following application, slabs were removed from the sprayer apparatus and placed in an opaque storage/transport container for drying, where it was kept level at all times to prevent runoff of the material applied. Each slab was allowed to fully dry with the lid of the container off.

e. Water Sample Preparation

After rainfall simulation, collected samples were weighted and preserved by the addition of 0.8 mL of 10% formic acid per bottle to reduce the pH of the water, and then reweighted. Similarly, three 1.5 L transit stability tap water samples, spiked at 1.03 µg/L and three blank samples, were prepared on site on the day of the simulation and preserved with formic acid as indicated above. All samples were kept in wet ice and transported the next day to the analytical laboratory.

2. Analytical Procedures

All samples collected as part of the study were analyzed at the designated analytical laboratory using a gas chromatography-negative chemical ionization mass spectrometry (GC-MS/NCI) (method RAAAYO26). Cypermethrin water samples were partitioned with dichloromethane thrice, concentrated to dryness and dissolved in an internal standard solution of deuterated standard (cyfluthrin-methyl-*d6*). The Limit of Quantitation (LOQ) was 1.03 ppb, stated to be equivalent to ~0.01% of the applied cypermethrin. The method was validated in the laboratory using samples spiked at 1.03 and 10.3 ppb (5 samples each) with an overall recovery of 102% and relative standard deviation was 3% (p. 127). According to the report, the method was linear through 517 ppb (p. 126). Further, during analysis laboratory samples were spiked at 10.3 µg/L with recoveries of 92% (average of 9 spiked samples) and relative standard deviation of 1%, which is in contrast with the recoveries of the transit stability samples (p. 122) (see also Section B of this DER). The limit of detection (LOD was not provided in the report.

II. Results and Discussion

A. Findings

Tables 3 and 4 present the results of the building material washoff study for Cynoff® WP and Cynoff ® EC formulations, respectively, presented in terms of percent of applied cypermethrin . Results in the

tables are ranked by mean percent washoff (high to low), with the greatest mean percent washoff reported from the clean vinyl siding (CVL) slabs in both formulations, and the lowest mean percent washoff reports from the clean unpainted concrete (CUC) or the clean unpainted stucco (CUS). Based on the application monitoring samples taken at the time of applications, cypermethrin was applied at 150% and 127% of the target application for the WP and EC formulations respectively (target for WP formulation was 28.1 mg; target for EC formulation was 26.5 mg). Rainfall simulator delivered consistent uniform rainfall events with an intensity of one-inch-per-hour.

Table 3. Building Material Washoff Results for Cynoff® WP in Terms of Percent of Applied Cypermethrin (ranked by mean percent washoff)

Slab Type	Simulation event 1, Replicate 1	Simulation event 2, Replicate 2	Simulation event 3, Replicate 3	Mean percent washoff (STDEV)
CVL	11.26	2.97	4.69	**6.31 (4.38)**
CAL	4.14	2.02	5.72	**3.96 (1.96)**
CUW	3.49	3.94	1.40	**2.94 (1.34)**
CUC	2.59	0.55	1.65	**1.60 (1.02)**
ASP	0.27	1.33	0.51	**0.70 (0.56)**
DPW	0.58	0.83	0.57	**0.66 (0.15)**
CPW	0.31	0.53	0.45	**0.43 (0.11)**
CPS	0.15	0.23	0.33	**0.24 (0.09)**
CUS	0.04	0.02	0.07	**0.04 (0.03)**
CPC	0.10	0.06	0.08	**0.08 (0.02)**
CAL (control)	--	--	--	--

Table 4. Building Material Washoff Results for Cynoff® EC in Terms of Percent of Applied Cypermethrin (ranked by mean percent washoff)

Slab Type	Simulation event 1, Replicate 1	Simulation event 2, Replicate 2	Simulation event 3, Replicate 3	Mean percent washoff (STDEV)
CVL	16.77	14.32	11.58	**14.22 (2.60)**
CUW	1.02	1.96	1.90	**1.63 (0.53)**
CAL	0.50	1.16	1.94	**1.20 (0.72)**
DPW	0.45	0.20	0.31	**0.32 (0.13)**
CUC	0.16	0.19	0.08	**0.14 (0.06)**
CPW	0.18	0.08	0.08	**0.11 (0.06)**
ASP	0.15	0.03	0.07	**0.08 (0.06)**
CPC	0.07	0.05	0.08	**0.07 (0.02)**
CPS	0.04	0.04	0.04	**0.04 (0.00)**
CUS	<0.01	0.01	<0.01	**0.01 (--)**
CAL (control)	--	--	--	--

Based on the results presented in Tables 3 and 4 clean vinyl siding (CVL) had the highest percent cypermethrin washoff (maximum 11.3% and 16.8% from WP and EC formulations, respectively). The next highest washoff resulted from clean aluminum siding (CAL; maximum 5.74% and 1.94% from WP and EC, respectively) and clean unpainted wood (CUW; maximum 3.94% and 1.96% from WP and EC, respectively). The lowest amount of washoff, as percent of applied cypermethrin, came from clean unpainted stucco (CUS) followed by clean painted stucco (CPS), clean painted concrete (CPC) or clean asphalt (ASP).

Control samples from clean aluminum siding were analyzed to have cypermethrin concentrations in the washoff samples less than the LOQ (1.03 ppb).

It should be noted that there was some variability between treatment groups for each formulation. The study authors propose that it was likely due to differences in the runoff volume collected per slab due to position within the rainfall simulator and differences in the final mass that dried on the surface following application. Slab locations were randomly selected and three treatment groups were performed for each formulation. It is important to note that for slabs which occupied the same position more than one time showed total runoff volumes that were within 6%.

B. Stability of Transported Samples

Three field spiked samples were analyzed to test for stability during transportation from treatment site to the analytical facility. Samples were spiked with a nominal concentration of 1.03 ppb (*i.e,* at the LOQ). Percent recovery ranged from 49 to 62%; 9 to 12% of the spiked chemical was found on the walls of the sample container. Table 5 below presents the results from the field spike analysis.

Table 5. Transit Stability Sample Results

Sample ID Number	Water Volume, L	Spiked Mass, ug	ug in Water	ug in Empty Bottle	Total ug Found	% of Spiked Mass
RS-TS-NA-NA-S-4A-A1	1.5	1.545	0.735	0.078	0.813	53
RS-TS-NA-NA-S-5A-A1	1.5	1.545	0.855	0.097	0.952	62
RS-TS-NA-NA-S-6A-A1	1.5	1.545	0.675	0.084	0.759	49

C. Statistical Analysis

The study authors performed a statistical analysis on both formulations that included a one-way ANOVA (Analysis of Variance) procedure and Dunnet's and Tukey's multiple comparison methods (MCM). The results of the ANOVA tests, confirmed by the study reviewer, indicated that there was significant difference between at least one slab type for mean washoff percent (significance at 0.0001 for the EC formulation and 0.001 for the WP formulation). The null hypothesis – mean percentages were equal for all slab types – was rejected for both formulations. It is important to note that greater variance was observed within each slab type as greater mean percent washoff was reported. Statistical analyses completed by the study authors are presented in Table 14 of the study report on page 39.

III. Study Deficiencies and Reviewer's Comments

Deficiencies:

1. Field spike sample recoveries were low (49-62%). The study authors report 9-12% of the spike mass was adsorbed to the shipping container. It is notable that if this amount is quantifiable it should be extractable. Also the recoveries for transit samples are low enough that it questions the stability of the test material in the runoff samples from the test slabs. Further field spikes were spiked with a nominal concentration equal to the LOQ. Spiked sample concentrations should have been greater than the LOQ.

Comments:

1. Some of the variance observed in the mean concentration may be attributed to the transport between the pesticide application site and the site of the rainfall simulator.

2. Drying of the slabs following application may have resulted in some amount of degradation. The study authors noted that some amount of applied mass was lost to the aluminum siding borders or to the runoff catch container when the slabs were moved from the track sprayer to the drying site.

3. Although recoveries of the field spiked samples were low, the study authors stated that the results should not impact the conclusions of the study as it was conducted as a comparative study to understand the relative propensities for a compound to washoff a range of hard surfaces, thus absolute concentrations are not critical to the study conclusions.

4. In order to prevent hydrolysis under alkaline conditions (tap water pH of study was 8.5-9.0) of cypermethrin following application, test slab were soaked in tap water with small amount of muriatic acid (HCl) to lower the pH prior to application of test material.

5. Application of test material was 127% and 150% of the target application for the EC and WP formulations, respectively.

6. Tank mix solutions were analyzed for cypermethrin content. For the EC formulation, the recoveries were 71-75% of the expected concentration (2.00 mg/L in solution) and for the WP formulation they ranged from 84-86%.

7. The transit stability samples were spiked at 1.03 ppb, which is around ¼ the solubility limit of 3.97 ppb in water. According to the submission, the transit stability spiked concentration was from one tenth to one thousandth of the observed water concentrations. Water samples from the slabs washoff contained up to 3556 ppb (p. 130-132). Therefore, the water concentrations greatly exceeded the solubility of cypermethrin in water. The formulation might have played an effect on the levels of cypermethrin in the water.

8. The method "had a standard curve between 7.23 and 207 µg/L. This range is equivalent to 0.36 to 10.4 µg/L (ppb) in the washoff samples."

9. Runoff volumes were highly variable 296.2-2140.4 g (0.2962-2.1404 L) (p. 130-132).